Geometry and Electronic Structure of the Hydroperoxyl Radical[1]

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Abstract: *Ab initio* self-consistent-field (SCF) and configuration-interaction (CI) calculations have been carried out to investigate the geometry and electronic structure of the $^2A''$ ground state of the HO_2 radical. A slightly better than double-ζ basis set of contracted Gaussian functions was used. First-order wave functions including 500 configurations were used to describe electron correlation in HO_2. The iterative natural orbital procedure was used to generate an optimum set of molecular orbitals. The SCF predicted geometry is r(H–O) = 0.968 Å, r(O–O) = 1.384 Å, and bond angle 106.8°. The first-order geometry is r(O–H) = 0.973 Å, r(O–O) = 1.458 Å, and bond angle 104.6°. Our bond angle is consistent with Walsh's prediction, and the overall geometry is in essential accord with that suggested by Paukert and Johnston. However, several earlier theoretical predictions are not consistent with our results. Force constants are predicted which suggest that the O–H bond is similar to that in water, but the O–O bond is much weaker than that in the O_2 molecule. The H–O_2 dissociation energy is predicted to 2.36 eV in the SCF approximation and 2.82 eV from CI, compared to an experimental value of 2 eV. The electronic structure of HO_2 is discussed in terms of the natural orbital occupation numbers and the most important configurations.

The HO_2 radical has long been considered to be an important intermediate in chemical reactions involving hydrogen and oxygen.[2-5] The first direct observation of HO_2 appears to be that of Foner and Hudson,[6] who generated the radical by the termolecular reaction between hydrogen atom, oxygen molecule, and a third body. Numerous other observations of HO_2 confirmed[7-9] that of Foner and Hudson.[6] HO_2 has been spectroscopically observed *via* matrix isolation by Milligan and Jacox[10] and by Ogilvie.[11] Only very recently has the gas-phase absorption spectrum of HO_2 been observed by Paukert and Johnston[12] using molecular modulation spectroscopy.[13]

Our theoretical interest in HO_2 centers around the fact that, despite the importance[14] of HO_2, its geometry has not been determined experimentally. The work of Milligan and Jacox[10] shows that, in an argon matrix at 4°K, the HO_2 radical is of C_s symmetry. The vibration spectrum determined by Paukert and Johnston for gaseous HO_2 is consistent with[12] (but does not uniquely determine) the geometry in which the H–O bond distance is 0.96 Å, the O–O bond distance is 1.3 Å, and the H–O–O angle is approximately 108°.

Several qualitative discussions[15-17] and one semiempirical[18] and one nonempirical treatment[19] have been concerned with the HO_2 geometry. Walsh[15] predicted a bond angle greater than 90° and slightly less than that of HNO, for which the H–N–O angle is now known[20] to be 108.5°. Green and Linnett[16] used an argument based on a $^3/_2$ bond order for O_2^- to predict an HO_2 bond angle of between 55° and 70°. Gimarc[17] has recently suggested that both the ground and excited states of HO_2 should be bent, since at least one electron will occupy the 7a′ orbital. Gordon and Pople[18] have carried out semiempirical INDO calculations which predict r(H–O) = 1.05 Å, r(O–O) = 1.19 Å, and θ = 110.7°. Finally, Boyd[19] carried out minimum-basis-set self-consistent-field (SCF) calculations on HO_2, predicting a C_{2v} geometry with a bond angle of 47°.

Ab initio theoretical treatments of electronic structure have now progressed to the point where it should be possible to make a reliable prediction of the geometries of small polyatomic molecules. For example, calculations similar to those reported here predicted[21] the triplet ground state of CH_2 to be bent, with an angle of 135°, prior to the experimental determination[22] of 136 ± 8°. In particular, we have found[23] that electron correlation[24,25] can be adequately treated using "first-order" wave functions[26] obtained using the iterative natural orbital (INO) procedure.[27] Therefore, the goal of the present research was to make a reliable prediction of the geometry of HO_2 and shed some light on the electronic structure of this molecule.

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Theoretical Approach

The basis set used is analogous to that used in previous calculations on methylene[21] except that three, rather than two, s functions on hydrogen were used. The 4s2p Dunning contraction[28] of Huzinaga's 9s5p primitive Gaussian basis[29] was used for each oxygen atom. Huzinaga's 5s set on hydrogen[29] was contracted to three functions by a 311 grouping. Thus, for C_s symmetry, our basis set consists of 19a′ and 4a″ contracted Gaussian functions.

Two types of *ab initio* calculations are reported here for the ground state of HO_2: (1) SCF, in which $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''$ is the dominant configuration for the $^2A''$ ground state, and (2) the approximate first-order wave function[23,26] within our basis.

The first-order wave function[23,26,30] is a particular type of configuration-interaction wave function which places special importance on the valence orbitals not occupied in the self-consistent-field approximation. To make this clear, consider a very simple case, the hydrogen molecule. The SCF or Hartree–Fock wave function for the ground state arises from the $1\sigma_g{}^2$ electron configuration. However, the $1\sigma_u$ molecular orbital can also be constructed from 1s atomic orbitals on each atom. Therefore, the $1\sigma_u$ orbital is central in determining the form of our first-order wave function. In addition to the SCF configuration, then, the first-order wave function for H_2 contains the following three types of configurations. (a) One type is single excitations, of the type $1\sigma_g \rightarrow n\sigma_g$. This excitation notation implies a configuration $1\sigma_g n\sigma_g$, where $n\sigma_g$ includes all the remaining (besides $1\sigma_g$) σ_g orbitals in the basis set. Configurations of this type may have a significant effect on calculated molecular properties, *e.g.*, dipole moments. (b) Also contained in this wave function are double excitations into the nonoccupied valence orbitals. $1\sigma_g{}^2 \rightarrow 1\sigma_u{}^2$, which is just the $1\sigma_u{}^2$ configuration, is the only configuration of this type for H_2. Configurations of this type are usually the most important energetically in first-order wave functions. (c) Finally, the wave function contains double excitations into one valence orbital and one other orbital. Configurations of this type for H_2 are $1\sigma_g{}^2 \rightarrow 1\sigma_u n\sigma_u$, or, more explicitly, $1\sigma_u 2\sigma_u$, $1\sigma_u 3\sigma_u$, $1\sigma_u 4\sigma_u$, ...

In principle, for the ground state of HO_2, the valence orbitals not occupied in the SCF approximation are 8a′ and 9a′. In addition, the 2a″ orbital is of particular importance since it is only singly occupied in the SCF configuration. However, for reasons of economy (and the fact that the $3\sigma_u$ orbital of O_2 is unimportant near r_e[23]), we have chosen *not* to consider the 9a′ as a valence orbital (in the sense described above) in the present work. In addition, the 1a′, 2a′, 3a′, and 4a′ (corresponding roughly to the 1s and 2s orbitals on oxygen) are held doubly occupied in all configurations. With the above two restrictions, our first-order wave functions contain 500 configurations, listed in Table I. The three general types of configurations (a, b, and c) above are separated by spaces in Table I.

The calculations proceeded in three steps: (1) computation of the SCF wave function, (2) generation of a set of additional (besides the SCF) orbitals which describe the single particle excited states of $HO_2{}^+$ (the a′ orbitals of this type are obtained from a calculation involving the 12 configurations $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a' na' 1a''^2$ where $n = 8, 9, 10, \ldots, 19$), (3) natural orbital iterations[27] on our 500 configuration wave function until the energy lowering was less than 1×10^{-5} hartree. In all cases, the INO procedure was reasonably well behaved. For large values (2.9, 3.0 bohrs) of the O–O distance, the total energy reached a minimum on the first INO iteration.

Table I. Configurations in the Approximate First-Order Wave Functions for the $^2A''$ State of HO_2[a]

Type excitation	$^2A''$ config per orbital occupancy	Total config
$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''$	1	1
$5a', 6a', 7a' \longrightarrow 8a', 9a', \ldots, 19a'$	2	72
$1a'' \longrightarrow 2a'', 3a'', 4a''$	2	6
$2a'' \longrightarrow 3a'', 4a''$	1	2
$5a'^2, 6a'^2, 7a'^2 \longrightarrow 8a'^2$	1	3
$5a'6a', 5a'7a', 6a'7a' \longrightarrow 8a'^2$	2	6
$5a'1a'', 6a'1a'', 7a'1a'' \longrightarrow 8a'2a''$	2	6
$1a''^2 \longrightarrow 8a'^2$	1	1
$1a''2a'' \longrightarrow 8a'^2$	1	1
$5a'^2, 6a'^2, 7a'^2, 1a''^2 \longrightarrow 8a'9a', \ldots, 8a'19a'$	2	88
$5a'^2, 6a'^2, 7a'^2, 1a''^2 \longrightarrow 2a''3a'', 2a''4a''$	1	8
$5a'6a', 5a'7a', 6a'7a' \longrightarrow 8a'9a', \ldots, 8a'19a'$	5	165
$5a'6a', 5a'7a', 6a'7a' \longrightarrow 2a''3a'', 2a''4a''$	2	12
$1a''2a'' \longrightarrow 8a'9a', \ldots, 8a'19a'$	2	22
$5a'1a'', 6a'1a'', 7a'1a'' \longrightarrow 8a'3a'', 8a'4a''$	5	30
$5a'1a'', 6a'1a'', 7a'1a'' \longrightarrow 9a'2a'', \ldots, 19a'2a''$	2	66
$5a'2a'', 6a'2a'', 7a'2a'' \longrightarrow 8a'3a'', 8a'4a''$	2	12
Total		500

[a] Most orbital occupancies give rise to more than one linearly independent doublet ($S = 1/2$) spin eigenfunctions. For a discussion of spin eigenfunctions, see R. Pauncz, "Alternate Molecular Orbital Theory," W. B. Saunders, Philadelphia, Pa., 1967.

Geometry and Force Constants

A number of preliminary SCF calculations with a coarse grid indicated that the equilibrium geometry was near $r(\text{H–O}) = 1.8$ bohrs, $r(\text{O–O}) = 2.8$ bohrs, $\theta = 110°$. Given this information, a finer grid was adopted, resulting in the calculated total energies given in Table II. Our *ab initio* points were least squares fit to the quadratic form

$$E = E_0 + k_{OH}[r(OH) - r_e(OH)]^2 + k_{OO}[r(OO) - r_e(OO)]^2 + k_\theta[\theta - \theta_e]^2$$

to determine the predicted minimum energy, geometry, and force constants. Our results are seen in Table III. The bending force constant K_θ has been divided by the product of the OH and OO equilibrium separations.

The bond angle including electron correlation is slightly less than the SCF value. Both of our predictions are in harmony with Walsh's opinion[15] that the

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Table II. Calculated HO_2 Energies (Hartrees) and Bond Distances (Bohrs)[a]

r(H–O)	r(O–O)	θ	SCF	First order
1.8	3.0	110	−150.13520	−150.23546
1.8	2.8	110	−150.15090	−150.24299
1.8	2.4	110	−150.15009	−150.22473
2.0	2.6	110	−150.14961	−150.23471
1.6	2.6	110	−150.14331	−150.22656
1.8	2.6	120	−150.15293	−150.23641
1.8	2.6	100	−150.15621	−150.24138
1.8	2.6	110	−150.15834	−150.24237
1.8	2.8	100	−150.15140	−150.24445
1.8	2.8	90	−150.14427	−150.23934
1.8	3.0	100	−150.13744	−150.23915
2.0	2.8	100	−150.14302	−150.23701
1.8	2.9	100	−150.14525	−150.24211

[a] 1 hartree = 27.21 eV; 1 bohr = 0.5292 Å.

Table III. Predicted Geometries and Force Constants for HO_2[a]

	SCF	First order
Minimum energy, hartrees	−150.1579	−150.2448
O–H bond distance, Å	0.968	0.973
O–O bond distance, Å	1.384	1.458
Bond angle, deg	106.8	104.6
k_{OH}	8.49	8.56
k_{OO}	4.65	2.51
k_θ	0.61	0.47

[a] Force constants are given in millidynes per ångström.

bond angle should be slightly less than that found in HNO,[20] 108.5°. Our angle of 104.6° differs by only 6.1° from that predicted using INDO,[18] but differs qualitatively from the predictions of Green and Linnett[16] and of Boyd.[19]

Our predicted OH bond distances, 0.968 Å (SCF) and 0.973 Å (CI), are very close to that observed experimentally,[31] 0.97 Å, for the $^2\Pi$ ground state of the OH radical. Pople and Gordon[18] predicted 1.05 Å for this bond distance.

The present calculations predict O–O bond distances of 1.384 Å (SCF) and 1.458 Å (CI). A similar relationship between SCF and CI bond distances was found[23] for O_2, where the first-order bond distance was 0.068 Å longer than the SCF value. Our predicted CI bond distance is much closer to that of H_2O_2 (1.475 Å)[32] than that of diatomic O_2 (1.207 Å).[31] In this respect the HO_2 radical is similar to hydrogen peroxide. Both SCF and CI O–O distances are in serious disagreement with the semiempirical prediction of Gordon and Pople,[18] 1.19 Å.

All three predicted geometrical parameters are in essential agreement with those suggested by Paukert and Johnston.[12] The largest discrepancy between our predictions and the Paukert–Johnston work is for the O–O bond distance, which we predict to be ~0.1 Å longer.

For the water molecule, first-order wave functions gave[33] the bending and stretching force constants to within 10% of experiment.[34] However, in that work[33] a larger basis set including polarization functions (d functions on oxygen and p functions on hydrogen) was used. Therefore, it is difficult to assess the accuracy of the force constants predicted here. Our H–O stretching force constant is 8.56 mdyn/Å, very close to the experimental value for H_2O,[34] 8.4 mdyn/Å, and somewhat larger than that for the OH radical,[31] 7.8 mdyn/Å. We tend to conclude that the OH bond in OH_2 is rather similar to that in H_2O and OH. The O–O stretching force constant is nearly twice as large in our SCF calculation as in the configuration-interaction treatment. Our predicted O–O force constants are about two and four times less than that known for O_2 in its ground state,[31] 11.8 mdyn/Å. The calculations thus imply that the O–O bond in HO_2 is much weaker than that in the X $^3\Sigma_g^-$ state of diatomic O_2. And, in fact, the O–O dissociation energy in HO_2 is thought to be ~2.7 eV,[35] only about half the dissociation energy of O_2, for which D_0 = 5.115 eV.[36] For the bending force constant, the inclusion of electron correlation also lowers the predicted value, from 0.61 to 0.47 mdyn/Å. Both predicted bending force constants are less than that for H_2O,[34] 0.76 mdyn/Å. Although it would be very interesting to compare our predicted HO_2 force constants to those of hydrogen peroxide, it does not appear that force constants have been determined experimentally for H_2O_2.

Analogous Calculations on O_2

Corresponding calculations on O_2 have been carried out to help calibrate our HO_2 results and to predict the H–O_2 dissociation energy. The SCF calculations yielded a minimum energy of −149.5712 hartrees at r = 1.212 Å, with a stretching force constant of 14.42 mdyn/Å. The first-order calculations gave an equilibrium internuclear separation of 1.245 Å, minimum energy of −149.6413 hartrees, and force constant of 14.19 mdyn/Å. For comparison, the experimental O_2 bond distance and force constant are[31] 1.207 Å and 11.8 mdyn/Å. It should be noted that the more accurate (including d functions) earlier computed[23] first-order wave function for O_2 gave much closer agreement with experiment for both r_e and the force constant.

Enlarging our present basis set would lower the SCF bond distance to the Hartree–Fock value,[37] 1.152 Å, which is a full 0.055 Å less than experiment. Nevertheless, in light of the known inadequacy of our basis set, it seems likely that the O–O distance in HO_2 is more accurately predicted by our SCF calculation than our energetically superior CI treatment.

The H–O_2 dissociation energy is predicted to be 2.36 eV from SCF and 2.82 eV from first-order calculations. We have found first-order dissociation energies to be quite reliable when large basis sets are used.[23] However, the smaller basis set used here is not likely to be as reliable. Experimentally, Foner and Hudson[9] have determined the H–O_2 dissociation energy to be ~2 eV, in fair agreement with both of our predictions.

Electronic Structure Considerations

Although at first sight a 500-configuration wave function might seem difficult to interpret, there are two rela-

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Table IV. Important Configurations in the Approximate First-Order Wave Function for HO_2. The Geometry Is r(H–O) = 1.80, r(O–O) = 2.80, θ = 100°

	Excitation	Coefficient	Energy criterion, hartrees
1.	$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''$	0.9709	
2.	$7a'^2 \longrightarrow 8a'^2$	0.1419	0.0226
3.	$7a'1a'' \longrightarrow 8a'2a''$	0.1252	0.0153
4.	$6a'7a' \longrightarrow 8a'9a'$	0.0683	0.0082
5.	$5a'7a' \longrightarrow 8a'10a'$	0.0474	0.0043
6.	$1a'' \longrightarrow 3a''$	0.0516	0.0032
7.	$7a'2a'' \longrightarrow 8a'3a''$	0.0313	0.0030
8.	$7a'1a'' \longrightarrow 8a'3a''$	0.0396	0.0027
9.	$6a'1a'' \longrightarrow 9a'2a''$	0.0408	0.0022
10.	$7a'1a'' \longrightarrow 8a'4a''$	0.0305	0.0021

tively simple ways of looking at such a wave function. The first is through the natural orbital occupation numbers.[38] For a single-configuration wave function these occupation numbers will be 0, 1, or 2, depending on the number of electrons occupying each orbital. For multiconfiguration wave functions, the deviations of the occupation numbers from integer values can be thought of as representing the inadequacies of the SCF or Hartree–Fock approximation. The 1a′, 2a′, 3a′, and 4a′ occupation numbers resulting from our first-order wave function are exactly 2.0, since these orbitals are doubly occupied in all configurations. At the geometry yielding the lowest calculated energy, the 5a′, 6a′, and 7a′ occupation numbers are 1.996, 1.991, and 1.931, while the 1a″ and 2a″ occupation numbers are 1.974 and 1.017. The closeness of the above numbers to 1.0 and 2.0 indicates that the SCF approximation provides a good description of the electronic structure. The 7a′ and 1a″ orbitals are slightly less important in the CI than in the SCF calculation, while the 2a″ orbital is allowed to increase in importance by the inclusion of correlation. The 8a′, 9a′, 10a′, and 11a′ orbitals are much less important, having occupation numbers 0.0728, 0.0065, 0.0032, and 0.0003. Similarly, the 3a″ and 4a″ occupation numbers are 0.0065 and 0.0019. The fact that the 8a′ orbital is more than 10 times more important than the next non-SCF orbital justifies our original approximation concerning the form of the first-order wave function.

By using the iterative natural-orbital procedure,[27] we guarantee a rapidly convergent configuration-interaction expansion.[38] Therefore it is reasonable to single out the leading terms in our 500-configuration wave function. These are seen in Table IV for the geometry corresponding to our lowest calculated energy. The second and third configurations are quite important and involve only the valence orbital 8a′ in addition to the orbitals occupied in the SCF wave function. Also given in Table IV is an energy criterion, given by

$$E = \sum_i C_i^2(H_{ii} - H_{11})$$

where the sum goes over all $^2A''$ configurations arising from the given orbital occupancy. H_{ii} is a diagonal Hamiltonian matrix element. According to this criterion, the second configuration $7a'^2 \rightarrow 8a'^2$ results in an energy lowering of more than 0.5 eV. It is interesting to note that the ranking of important configurations based on the CI expansion coefficient differs by little from that based on the energy criterion.

Concluding Remarks

Ab initio SCF and configuration-interaction wave functions have been reported for the HO_2 radical, an important intermediate in numerous chemical reactions. The geometry predicted should be rather reliable. At some time in the future we hope to be able to investigate the first excited state of HO_2, which arises from the electron configuration $6a'^2 7a' 1a''^2 2a''^2$. Walsh[15] has suggested that this state should be low lying. The present calculations demonstrate with previous work[21,33,39] that properties of chemical interest can now be reliably predicted by first-principles electronic structure calculations which take electron correlation into account.

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(39) We have found first-order wave functions to yield reliable dissociation energies and geometries for several other molecules, including BH, BeO, KrF^+, H_2O, and NH_2.